



A single-ion gel polymer electrolyte system for improving cycle performance of LiMn₂O₄ battery at elevated temperatures



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ABSTRACT

The LiMn₂O₄ based lithium batteries using commercially available electrolytes suffer from poor cycling performance at elevated temperatures (above 55 °C). This is mainly caused by the Mn dissolution generated from HF thermally decomposed from the LiPF₆ salt at elevated temperatures. In this paper, a single-ion gel polymer electrolyte (polymeric lithium tartaric acid borate @ poly(vinylidene fluoride-co-hexafluoropropylene) was explored for improving the cycling performance of the LiMn₂O₄ based lithium battery at elevated temperatures owing to superior thermal stability and comparable ionic conductivity. It was manifested that the Li/LiMn₂O₄ cells using this single-ion gel polymer electrolyte showed stable charge/discharge voltage profiles, preferable rate capability and excellent cycling performance both at room temperature and elevated temperature of 55 °C. The dissolution of metallic Mn in this electrolyte is significantly suppressed than that of LiPF₆ electrolyte. These superior performances could endow this single-ion gel polymer electrolyte a promising alternative to the conventional liquid electrolyte system in the LiMn₂O₄ battery at elevated temperatures.

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1. Introduction

Spinel-type lithium manganese oxide (LiMn₂O₄) is one of the most promising cathode materials for large-format lithium ion batteries for electric vehicles (EV) due to its cost-effectiveness, facile production, high discharge voltage plateau (~4.0 V vs. Li/Li⁺) and environmental benignity compared to other cathode materials [1–3]. Moreover, the LiMn₂O₄ battery can deliver much higher energy density more than 200Wh/kg in order to meet the requirement of EV long driving ranges when compared to the corresponding lithium ion batteries (150Wh/kg). These features, especially, along with their low cost and environmental benignity, render them an attractive substitute for lead-acid batteries in battery-operated motor or EV. However, LiMn₂O₄ based battery suffers from poor cyclic capability, especially at elevated temperatures (above 55 °C) [1–10]. This drawback is mainly related to continuous growth of cell impedance and Mn dissolution caused

by the harmful components (LiF and HF) from the decomposing reaction of the LiPF₆ salt at elevated temperatures.

A variety of strategies have been taken to improve cycling capability of LiMn₂O₄ based electrodes such as doping [4–7], surface coating [8–13] and functional additives in the electrolyte [1,14–19] at elevated temperatures [20,21]. Ionic liquid-based electrolyte and single-ion-conducting nanocomposite polymer electrolytes are also very promising candidates to solve the LiMn₂O₄ cycling problems [22–24]. For example Al³⁺ doped spinel LiMn₂O₄ cathode exhibited excellent structural stability at elevated temperature [4–7]. Further, the VO_x, ZrO₂, Al₂O₃, or SiO₂ coated LiMn₂O₄ cathode exhibited interfacial stability at the elevated temperature as well and a significantly suppressed dissolution of Mn [10,11]. Recently, Prof. Lee reported that LiNi_{0.5}Mn_{1.5}O₄ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ spinel cathodes were coated with a polyimide polymer for effectively preventing the direct exposure of the LiNi_{0.5}Mn_{1.5}O₄ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ surface to liquid electrolyte [12,13]. In addition, 2-(triphenylphosphoranylidene) succinic anhydride was developed as an electrolyte additive to improve high temperature cycle performance of LiMn₂O₄/graphite Li-ion batteries due to its electrochemical decomposition and deposition on both surfaces of LiMn₂O₄ and graphite [17]. The above strategies would not in essence tackle the poor cyclic performance

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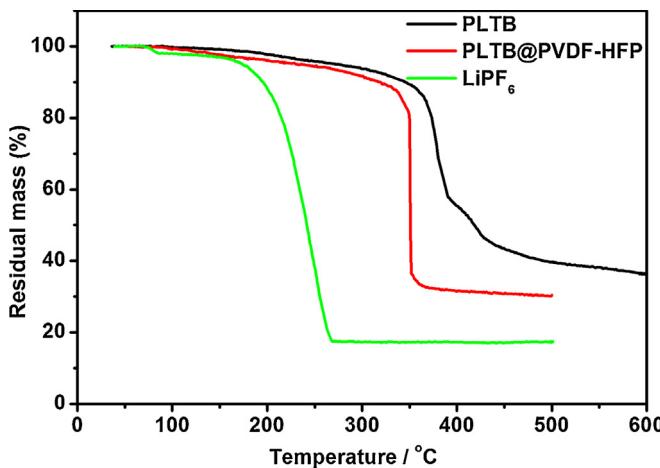


Fig. 1. Thermal gravimetric analysis curves of PLTB, PLTB@PVDF-HFP and LiPF₆.

of LiMn₂O₄ cathodes at elevated temperatures owing to the still involvement of thermally unstable LiPF₆ salt. So, a new electrolyte containing a thermally stable lithium salt was highly desirable to substitute LiPF₆-based electrolyte.

Some new lithium salts [21,27] were synthesized in the last few years, such as lithium bis(oxalato)borate (LiBOB), which presented superior thermal stability, considerable lithium ion transference number and fair dissociation constant. This type of lithium salt was possessed of boron as central atom, surrounded by four oxygen ligands to form a big π -conjugated system. The molecular configuration was helpful to delocalize the negative charge of the central ion, and the anion became more thermodynamically stable. Moreover, it was reported that the cell using LiBOB-based electrolyte maintained stable performance at elevated temperature due to excellent thermal stability and absence of HF [20,21]. Recently we reported a novel kind of “main-chain” type polymeric lithium tartaric acid borate, which possessed a

high thermal decomposition temperature at 330 °C. It was verified that the ethylene carbonate/dimethyl carbonate (EC/DMC) swollen polymeric lithium tartaric acid borate @ poly(vinylidene fluoride)-co-hexafluoropropylene (PLTB@PVDF-HFP) exhibited a superior ionic conductivity at room temperature ($\sigma = 0.50 \text{ mS cm}^{-1}$) and significantly high lithium ion transference number ($t_{\text{Li}^+} = 0.91$) [26]. In addition, the gel-like PLTB@PVDF-HFP electrolyte could play a positive role in preventing the generation of Li dendrite [25]. So, it was also anticipated to improve the elevated temperature cycle performance of LiMn₂O₄ cathodes. In order to explore the feasibility of using PLTB@PVDF-HFP in LiMn₂O₄ batteries, in this article, the cyclic capability and the rate discharge performance of LiMn₂O₄/Li cells using PLTB@PVDF-HFP based electrolyte were investigated in comparison with those of LiPF₆ based electrolyte at elevated temperatures.

2. Experimental

2.1. Materials

Ethylene carbonate (EC) and dimethyl carbonate (DMC) (all from Capchem Technology Co., Ltd), 1 M LiPF₆-EC/DMC (1/1, v/v, Guotai-huarong New Chemical Materials Co., Ltd.), PVDF-HFP (Aldrich, M_w~400,000, M_n~130,000, pellets, VDF:HFP~1:1), N, N-Dimethyl Formamide (DMF, 99.8%, superdry, J&K), LiMn₂O₄ (Hunan Reshine New Material Co., Ltd.) and PP separator (Celgard 2500). All materials were all commercially available and used without further purification.

2.2. Preparation and characterization of the PLTB-based electrolyte

The procedure for the synthesis of PLTB was presented in our previous work [25,26]. The preparation of PLTB@PVDF-HFP membranes are described briefly as follows. PLTB and PVDF-HFP were added into DMF(PLTB/PVDF-HFP = 1.0/1.0 (w/w), 25 μm) and mixed to be a transparent and homogeneous solution. Then the

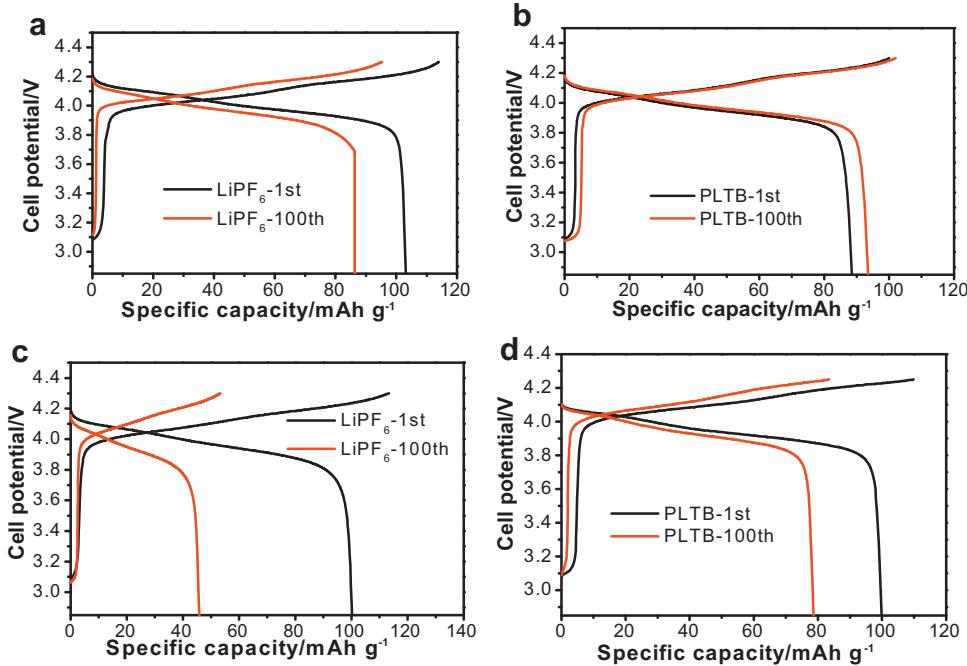


Fig. 2. The 1st and 100th charge and discharge curves of the Li/LiMn₂O₄ cells using LiPF₆ (a, c) and PLTB (b, d) based electrolytes respectively at room temperature (a, b) and elevated temperature of 55 °C(c, d).

PLTB@PVDF-HFP membranes were prepared by a doctor-blading process under ambient atmosphere followed by a vacuum drying at 70 °C to remove DMF. Finally, PLTB@PVDF-HFP membranes were immersed in mixed solvents EC/DMC (1/1, v/v) to obtain the solvents swollen PLTB@PVDF-HFP gel electrolyte. The weight ratio of PLTB/PVDF-HFP/(EC/DMC) was 0.50/0.50/2.0 (w/w/w). The thickness of the solvent swollen PLTB@PVDF-HFP membrane was ~75 μm. The surface morphology, the ionic conductivity, the electrochemical stability and lithium ion transference number of the solvents swollen PLTB@PVDF-HFP membrane were reported in our previous works [26].

2.3. Cells assembly and performance

The thermal behavior of PLTB, LiPF₆ and PLTB@PVDF-HFP were measured on thermo gravimetric analyzer (TGA, Rubotherm-DYNATHERM-HP) in a Al₂O₃ pan under an argon atmosphere at a heating rate of 10 °C min⁻¹. The Li/PLTB/LiMn₂O₄ and Li/LiPF₆/LiMn₂O₄ cells (2032-type) were assembled by sandwiching the PLTB and LiPF₆ based electrolytes between lithium metal foils and LiMn₂O₄ electrodes, respectively. The LiMn₂O₄ electrode was composed of 90 wt% LiMn₂O₄ (around 5.0 mg active material on 1.54 cm² aluminium metal foil), 5 wt% PVDF and 5 wt% carbon black. All assembly of cells was carried out in an argon-filled glove box. The charge/discharge profiles, C-rate capability and cycling ability of cells were recorded on a LAND battery test system. The galvanostatic charge/discharge behavior of Li/PLTB/LiMn₂O₄ and Li/LiPF₆/LiMn₂O₄ cells were conducted over the range of 2.75~4.25 V.

The AC impedance of the cells after 1st and 100th cycle at elevated temperature were analyzed using a Zahner Zennium electrochemical working station over a frequency range of 0.1–10⁶ Hz with a perturbation amplitude of 10 mV. The variation in electrode polarization during cycling was measured using cyclic voltammetry (CV). The surface morphology of the lithium metal foils and the LiMn₂O₄ cathodes after 100 cycles was observed by Hitachi S-4800 field emission scanning electron microscope (SEM). The element compositions on the LiMn₂O₄ cathodes were examined by energy dispersive X-ray spectroscopy (EDX, HoRIBA 7593-H) at a magnification of 5000 times and an accelerating voltage of 15.0 kV. Inductively coupled plasma mass spectrometry (ICP-MS, Thermo X7) was employed to analysis the Mn concentration in the electrolyte after the cell was cycled at elevated temperatures. The electrolyte collected from the cycled cell was rinsed in 10 mL concentrated HNO₃ solution and then diluted 1000 times for ICP-MS measurement.

3. Results and discussion

3.1. Thermal property of PLTB and PLTB@PVDF-HFP electrolyte

The thermal gravimetric analysis (TGA) curves of PLTB, PLTB@PVDF-HFP and LiPF₆ were shown in Fig. 1. It could be seen that LiPF₆ started a slight dissociation at around 70 °C and a rapid weight loss at 150 °C, whereas PLTB and PLTB@PVDF-HFP exhibited relatively higher thermal decomposition temperatures at 330 °C and 300 °C, respectively. It was verified that the PLTB salt possessed superior thermal stability compared with LiPF₆ salt.

3.2. Battery performance of Li/PLTB/LiMn₂O₄ battery

The charge/discharge curves of the Li/LiMn₂O₄ cells using LiPF₆ and PLTB based electrolytes at room temperature or elevated temperature at charge/discharge rate of 0.5 C (200 μAcm⁻²) were depicted in Fig. 2. Both cells exhibited stable charge/discharge curves and the charge/discharge plateaus were observed to be at

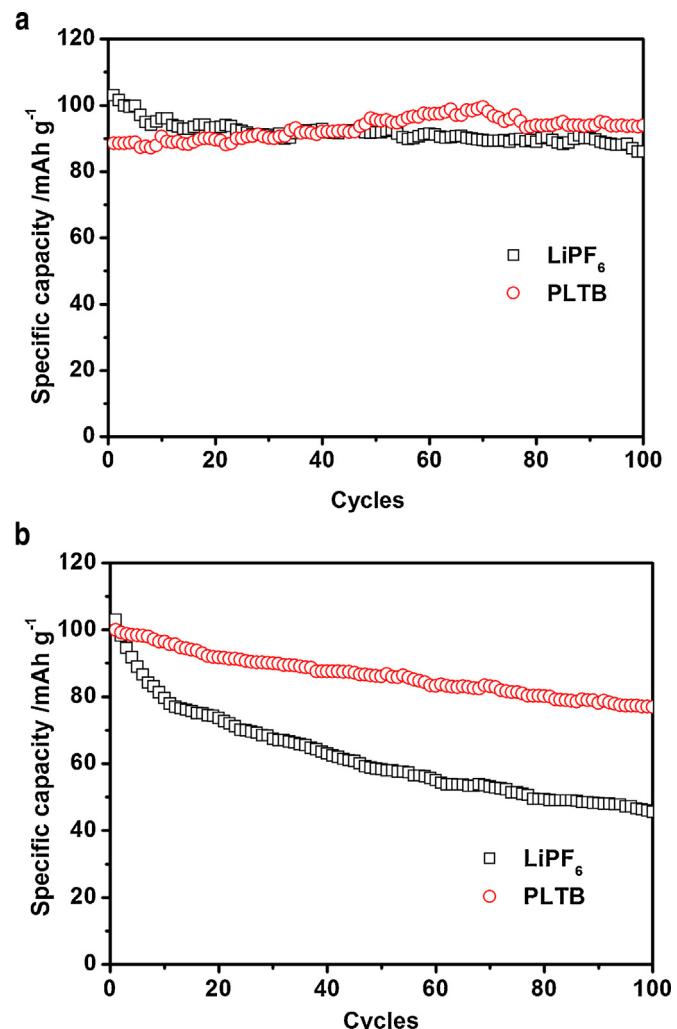


Fig. 3. The specific capacity versus cycle number curves of the cells using LiPF₆ and PLTB as electrolyte salts at room temperature (a) and at elevated temperature of 55 °C(b).

about 4.0 V vs Li/Li⁺ and 4.2 V vs Li/Li⁺ respectively, which were corresponding to the phase transformations of LiMn₂O₄ crystals. At room temperature, the cell using the LiPF₆-based electrolyte showed slow specific capacity fading from 103.0 mAhg⁻¹ to 86.5 mAhg⁻¹ with retention ratio of 83.4% after 100 cycles (seen in Fig. 3a). In comparison, the cell using PLTB-based electrolyte exhibited a slightly increasing specific capacity from 88.6 to 99.0 mAhg⁻¹ in the first 70 cycles owing to the activation at the interfaces between the gel electrolyte and the electrodes. After that, the cell using PLTB started to show slight capacity fading from 99.0 mAhg⁻¹ to 93.6 mAh g⁻¹ with a retention ratio of 90.9% (calculated on the initial capacity of 103.0 mAhg⁻¹) after 100 cycles. Therefore, the cell using the PLTB-based electrolyte just delivered a slightly better cycling performance at room temperature.

In sharp comparison, the specific capacity retentions of the two cells after 100 cycles became more pronounced at elevated temperature of 55 °C, as shown in Fig. 2(c-d) and Fig. 3b. The LiPF₆-based cell underwent rapid capacity deterioration from 100.5 mAhg⁻¹ to 45.6 mAhg⁻¹ with a retention ratio of 45.4%, which was consistent with previous reports by others [21]. By contrast, the cell using PLTB-based electrolyte exhibited a rather slow fading rate from 100.0 mAhg⁻¹ to 76.9 mAhg⁻¹ indicative of a much higher retention of 76.9%. These findings suggested that the Li/LiMn₂O₄

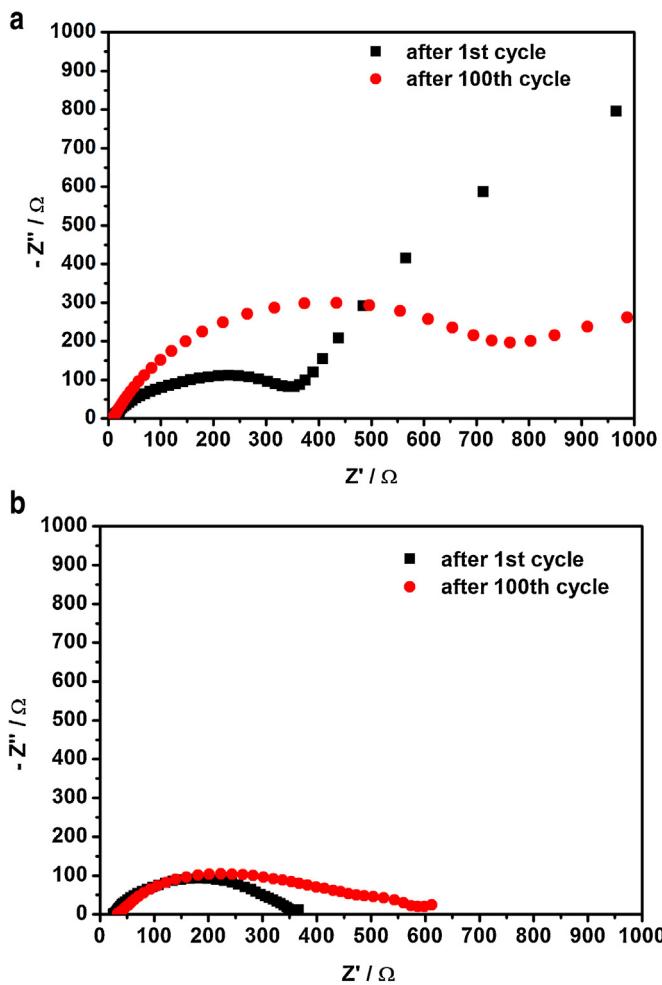


Fig. 4. AC impedance spectra of the cells using LiPF_6 (a) and PLTB (b) based electrolyte after the 1st and 100th charge/discharge cycle at the elevated temperature of 55 °C.

cells using PLTB-based electrolyte showed much improved cycling performance at the elevated temperature of 55 °C.

3.3. AC impedance analysis and CV analysis

In an effort to gain deep insight into the positive influence of the PLTB-based electrolyte on the cycling performance of LiMn_2O_4 electrodes, the AC impedance spectra of the cells after the 1st and 100th cycle at elevated temperature of 55 °C were depicted in Fig. 4. It was shown that the cell impedance of the LiPF_6 based electrolyte considerably increased from 343 Ω (1st cycle) to 764 Ω (100th cycle), while the cell impedance of the PLTB based electrolyte increased from 355 Ω (1st cycle) to 586 Ω (100th cycle). This indicated that the significant capacity fading of the LiPF_6 based cell during cycling was closely related to the increased interfacial resistance, which might result from the continuous electrolyte decomposition and formation of LiF. In a fair comparison, although the initial cell impedance for the PLTB-based electrolyte was slightly higher than that of the LiPF_6 based electrolyte, the growth of cell impedance was significantly retarded. This demonstrated that the PLTB based electrolyte may effectively alleviate the decomposition of liquid electrolyte and suppress the formation of LiF on the LiMn_2O_4 surface during high temperature cycling [12,13].

In addition to elucidation of the cell impedance augment, the variation in electrode polarization during cycling was also

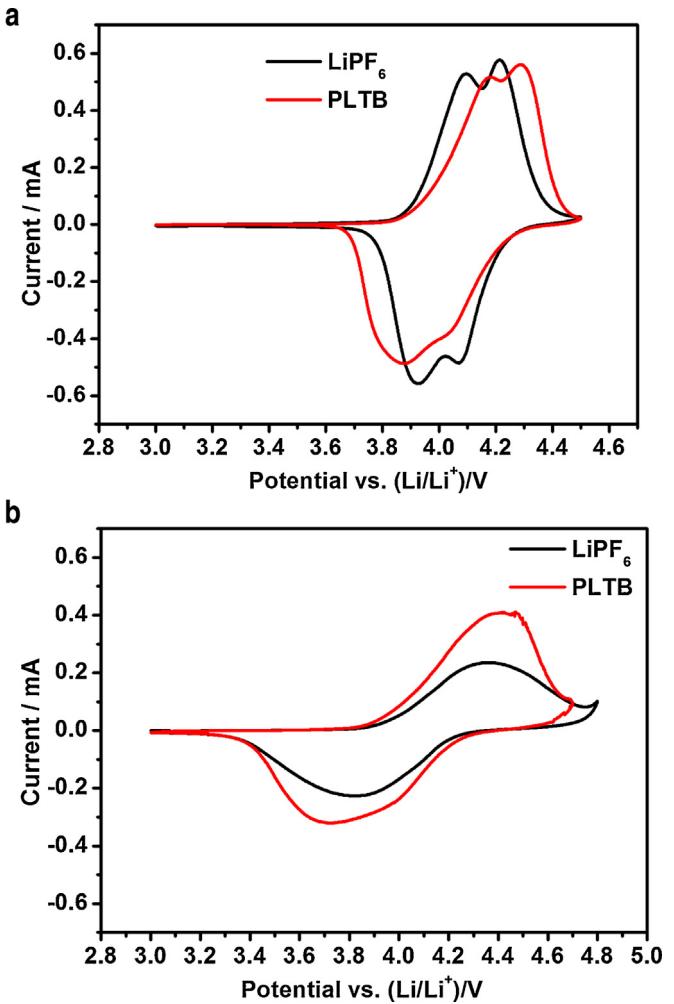


Fig. 5. Cyclic voltammograms of the LiMn_2O_4 cells using LiPF_6 and PLTB-based electrolytes after the 1st (a) and 100th (b) cycle at the elevated temperature of 55 °C (at a scan rate of 0.1 mV s⁻¹ under a voltage range of 3.0–4.5 V).

measured using cyclic voltammetry (CV). Herein, the cells were cycled at a scan rate of 0.1 mV s⁻¹ under a voltage range of 3.0–4.5 V. Fig. 5(a, b) showed the cyclic voltammograms of the LiMn_2O_4 cells using LiPF_6 and PLTB-based electrolytes after the 1st and 100th cycle at 55 °C. Similar to the previous results, two pairs of major redox peaks were observed. In cyclic voltammograms, the peak currents and potential separations of the redox were known to indicate the kinetics, wherein a lower peak current and larger potential separation represented stronger electrode polarization. In the case of LiPF_6 based electrolytes, the peak currents decreased from 0.54 mA to 0.23 mA and potential separations increased from 0.169 V (after the 1st cycle) to 0.528 V (after the 100th cycle). In comparison, the peak currents for the PLTB-based electrolyte were reduced from 0.51 mA to 0.41 mA and the growth of potential separations was from 0.354 V to 0.695 V. A quantitative comparison of these results confirmed that it was effective in preventing the formation of an undesired resistive layer hindering charge transport at the LiMn_2O_4 /liquid electrolyte interface in the PLTB-based electrolytes, which agreed well with the above results of the cell impedance.

3.4. SEM and ICP analysis

Fig. 6(a–c) showed the SEM images of the LiMn_2O_4 electrodes cycled in the PLTB-based electrolyte and the LiPF_6 -based electrolyte

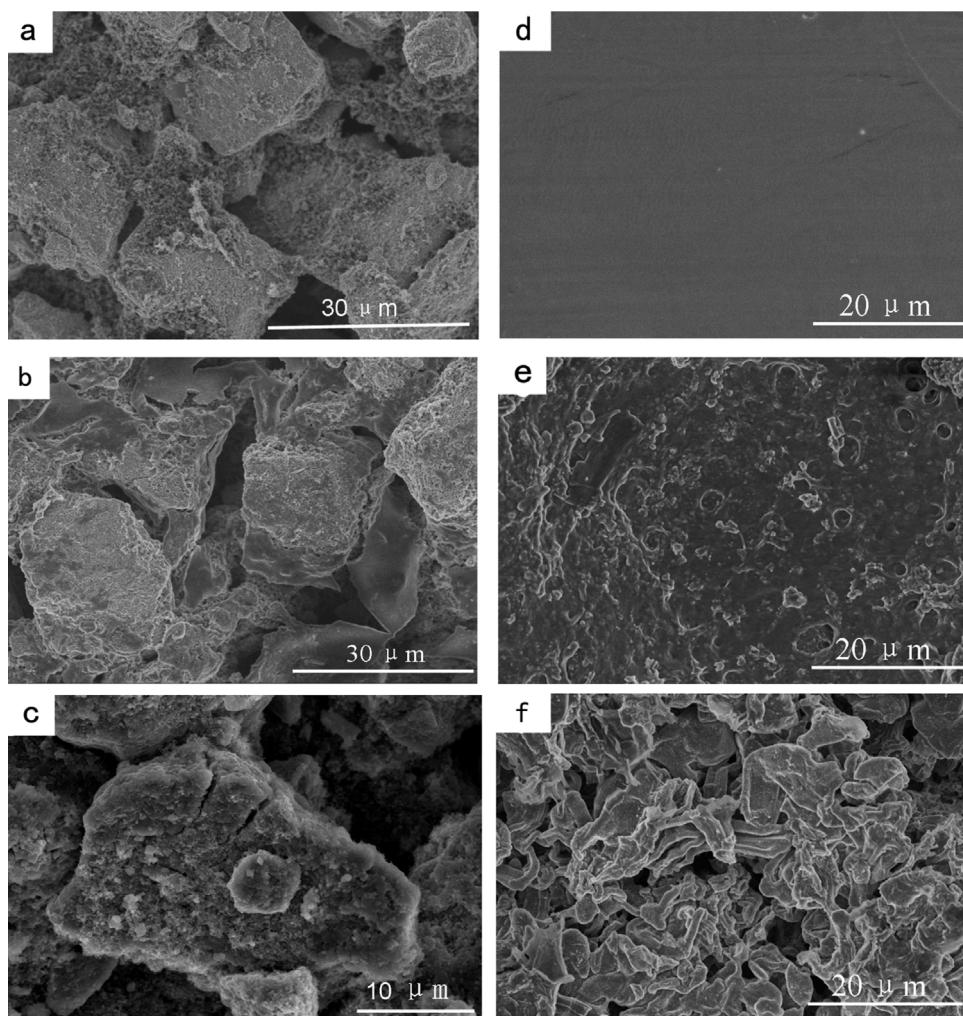


Fig. 6. SEM images of the pristine LiMn_2O_4 cathode (a), the LiMn_2O_4 cathodes cycled in the PLTB-based electrolyte (b) and cycled in the LiPF_6 -based electrolyte after 100 cycles at 55 °C (c), the pristine lithium foil anode (d), the lithium foil anodes cycled in the PLTB-based electrolyte (e) and cycled in the LiPF_6 -based electrolyte after 100 cycles at 55 °C (f), respectively.

after 100 cycles at 55 °C. The SEM image of the LiMn_2O_4 electrode in the PLTB-based electrolyte showed a smooth surface similar to the pristine electrode. By contrast, on the surface of the electrode in the LiPF_6 -based electrolyte, there were many cracks observed among the particles. This indicated that the PLTB-based electrolyte was stable and did not erode the electrode, thus allowing cells using PLTB based electrolyte to work satisfactorily at elevated temperatures; whereas, the electrode would be dissolved in the LiPF_6 electrolyte at the same elevated temperature. In order to further investigate the metallic Mn dissolution, ICP-MS was employed to analysis the concentration of the metallic Mn in the electrolytes after 50th cycle at the elevated temperature. The Mn concentration in the PLTB-based electrolyte was statistically averaged to be 8.4 ± 0.5 ppm, which was significantly lower than that of the LiPF_6 -based electrolyte (39.8 ± 0.8 ppm). EDX analysis corroborated a relatively higher concentration of Mn and a lower concentration of F on the surface of the LiMn_2O_4 cathode in PLTB-based electrolyte (seen in Table S1). These findings demonstrated that the LiMn_2O_4 cathode was more stable in the PLTB-based electrolyte than in the LiPF_6 -based electrolyte.

3.5. Lithium dendrites analysis

To give insight into the positive effect of PLTB-based electrolyte in preventing the generation of Li dendrites [28–32], the surface

morphology of lithium metal foils was studied by SEM observation after 100 cycles, which were depicted in Fig. 6(d–f). It was displayed in Fig. 6(d) that the surface of pristine lithium foil was rather smooth. However, the surface of lithium metal foil using LiPF_6 -based electrolyte became rather rough and was composed of a large amount of Li dendrites after 100 cycles at 55 °C. For the PLTB-based electrolyte, the surface of lithium metal foil was relatively smooth after 100 cycles indicating no obvious sign of Li dendrites when compared to that of LiPF_6 -based electrolyte. This may be due to the homogenous and gel-like PLTB@PVDF-HFP membrane which results in homogenous current density distribution [33–35].

4. Conclusions

In summary, it was manifested that PLTB@PVDF-HFP exhibited a superior thermal stability compared to that of the traditional LiPF_6 based electrolyte. The Li/Li Mn_2O_4 cells using the EC/DMC swollen PLTB@PVDF-HFP as polymer electrolyte demonstrated stable charge/discharge voltage profiles, preferable rate capability and excellent cycling performance both at room temperature and elevated temperature of 55 °C. Moreover, PLTB based electrolyte alleviated the growth of cell impedance and the Mn dissolution problem especially at elevated temperatures. These superior performances of EC/DMC swollen PLTB@PVDF-HFP could endow this

class of gel polymer electrolyte a very promising alternative to state of the art liquid electrolyte system in the LiMn_2O_4 lithium batteries.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2014.07.004>.

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